

Filled $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y$ skutterudites: processing and thermoelectric properties

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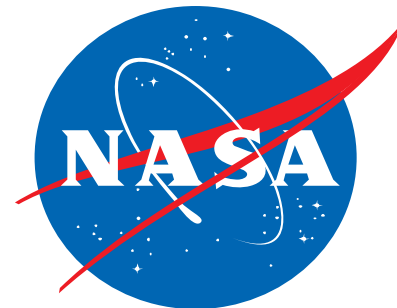
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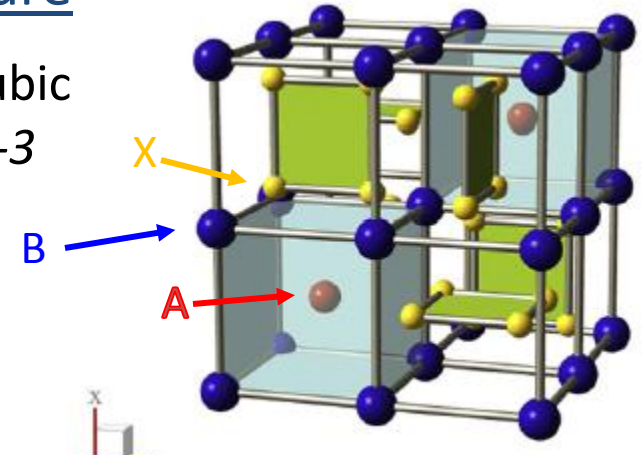
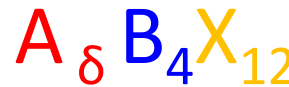


System Background

- Skutterudites are based on CoAs_3 mineral; first mined in Skutterud, Norway.
- Exhibit a high figure of merit for n-type systems ($ZT=1.7$).
- Relatively low cost system.
- Introduce a range of fillers (A) to scatter various phonon wavelengths.
- Introduce disorder on pnictogen ring sites (X).
 - Dominate heat carrying modes are associated with pnictogen vibration.
- Tune electronic properties (A,B,X) for optimal thermoelectric power factor .

Crystal Structure

Body-centered cubic space group $Im-3$



Eilertsen *et al.* Acta Mater. **60** (2012) 2178-2185.

Chi *et al.* Phys. Rev. B **86**: 195209 (2012).

																		$X' \ X \ X'$				
hydrogen 1 1.00794																	helium 2 4.002602					
lithium 3 6.941	beryllium 4 9.0122															boron 5 10.811	carbon 6 12.011	nitrogen 7 14.006	oxygen 8 15.999	fluorine 9 18.998	neon 10 20.180	
sodium 11 22.990	magnesium 12 24.305															aluminum 13 26.982	silicon 14 28.086	phosphorus 15 30.974	sulfur 16 32.06	chlorine 17 35.453	argon 18 39.948	
potassium 19 39.098	calcium 20 40.078	scandium 21 44.956	titanium 22 47.887	vanadium 23 50.942	chromium 24 51.996	manganese 25 54.938	iron 26 55.845	cobalt 27 58.933	nickel 28 58.693	copper 29 63.546	zinc 30 65.38	gallium 31 69.723	germanium 32 72.63	arsenic 33 74.922	selenium 34 78.96	bromine 35 79.904	krypton 36 83.80					
rubidium 37 85.468	strontium 38 87.62	ytrium 39 88.906	zirconium 40 91.224	niobium 41 92.906	molybdenum 42 95.94	technetium 43 [98]	ruthenium 44 101.07	rhodium 45 102.91	palladium 46 106.42	silver 47 107.87	cadmium 48 112.41	indium 49 114.82	tin 50 118.71	antimony 51 121.76	tellurium 52 127.6	iodine 53 126.90	xenon 54 131.29					
cesium 55 132.91	barium 56 137.33	57-70		lanthanum 57 138.91	cerium 58 140.12	praseodymium 59 140.91	neodymium 60 144.24	promethium 61 [145]	samarium 62 150.36	euroium 63 151.96	gadolinium 64 157.25	terbium 65 158.93	dysprosium 66 162.50	holmium 67 164.93	erbium 68 167.26	thulium 69 168.93	ytterbium 70 173.04					
francium 87 [223]	radium 88 [226]	89-102		actinium 89 [227]	thorium 90 232.04	protactinium 91 231.04	uranium 92 238.03	neptunium 93 [237]	plutonium 94 [244]	americium 95 [243]	curium 96 [247]	berkelium 97 [247]	californium 98 [251]	esbium 99 [252]	fermium 100 [257]	mendelevium 101 [258]	nobelium 102 [259]					
																		unilennium 114 [289]				

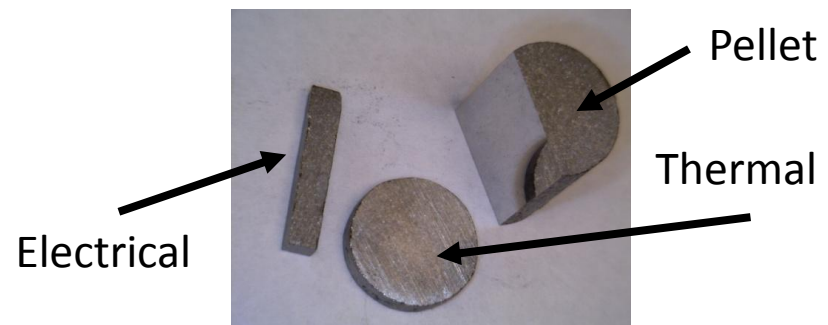
Skutterudite System Investigated

- Nd filled, Ge doped $\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ skutterudite, $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y$.
- Zhang *et al.* has previously investigated $\text{Nd}_{0.6}\text{Fe}_2\text{Co}_2\text{Sb}_{12-y}\text{Ge}_y$ system.
 - Reported peak p-type ZT 1.1 for $y=0.15$.
 - Reported formation of a nano-structured precipitate, reported to lower thermal conductivity and cause high ZT.
- Interested to expand the parameter space of Zhang's work.
 - Nd level $z = \{0 - 0.8\}$
 - Fe level $x = \{1, 2, 3\}$
 - Ge level $y = \{0, 0.15\}$

Zhang *et al.* J. Appl. Phys. **114** (2013).

Objectives

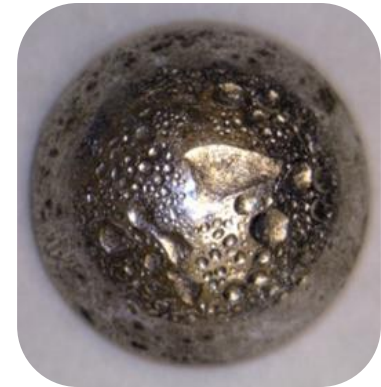
- Focus on finding a p-type skutterudite with improved ZT.
- Study thermoelectric behavior of the skutterudite $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y$.
- Study processing conditions.
- Study effect of composition on properties.
- Samples created from a melt/mill/hot press procedure.



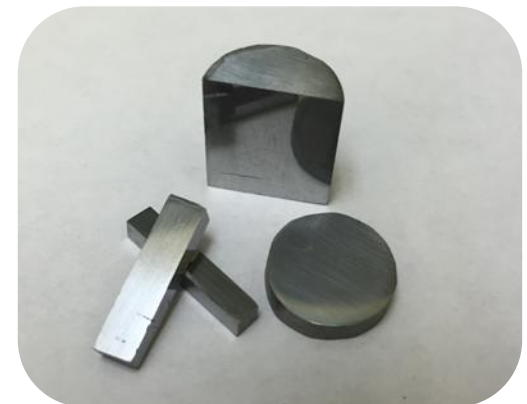
Processing Conditions

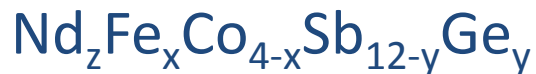
- Ingots were fabricated by solidification.
 - 1100°C for 1 hour
 - 10°C/min cooling rate
 - Ingot dimensions 1" diameter, 2" height
 - He atmosphere
 - Carbon crucibles
- Ingots crushed in mortar and pestle then milled.
 - Planetary ball mill
 - WC milling jar and media
 - 500 rpm for 3-6 hours
- Powder was consolidated in a hot press.
 - 520-575°C with 62 MPa for ½ hour
 - 1.5°C/min cooling rate
 - ½" graphite die, lined with grafoil
- All compositions were processed with identical conditions.

Solidified Ingot



Hot Pressed Pellet



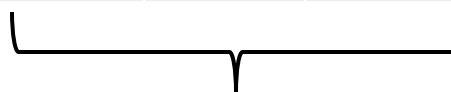


X-Ray Diffraction

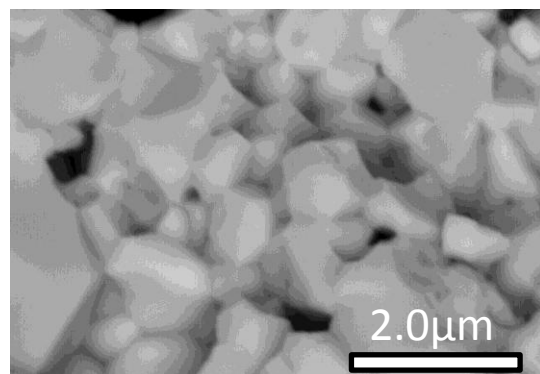
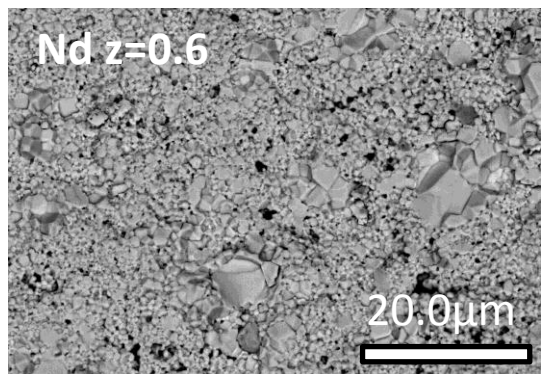
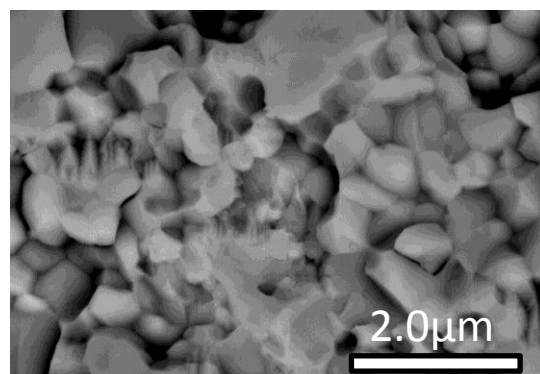
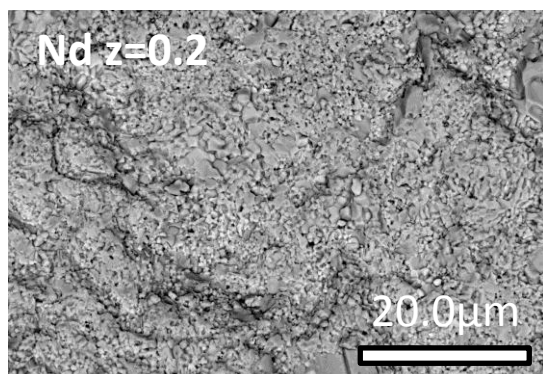
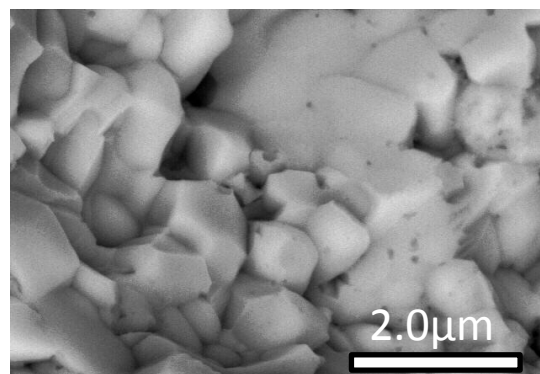
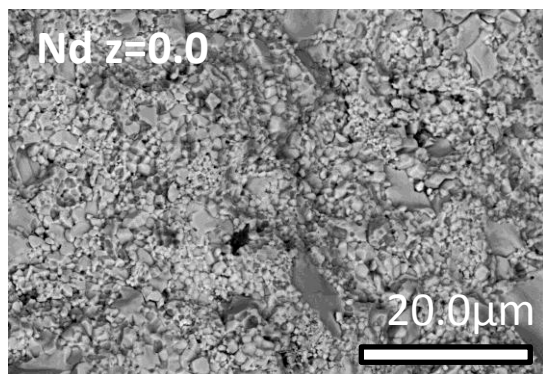
- Powder XRD of crushed pellets was evaluated with Rietveld refinement.
- Main phase is SKD structure, secondary phases include FeSb_2 and Sb.
- SKD phase purity decreases significantly for $\text{Nd} < 0.5$ and $\text{Fe} > 2$, no major impact from Ge.
- Filler occupancy increases with Nd level from 0 to 0.6 then levels off with maximum around 0.6.

X-Ray Diffraction Summary

Nd Level (z)	Fe Level (x)	Ge Level (y)	SKD Phase (wt%)	Filler Occupancy
0.0	2	0.15	57	0.00
0.2	2	0.15	62	0.16
0.4	2	0.15	66	0.23
0.5	2	0.15	87	0.45
0.6	2	0.15	100	0.62
0.7	2	0.15	95	0.52
0.8	2	0.15	96	0.60
0.6	3	0.15	57	0.67
0.6	2	0.15	100	0.62
0.6	1	0.15	100	0.27
0.6	2	0.00	90	0.43
0.6	2	0.15	100	0.62

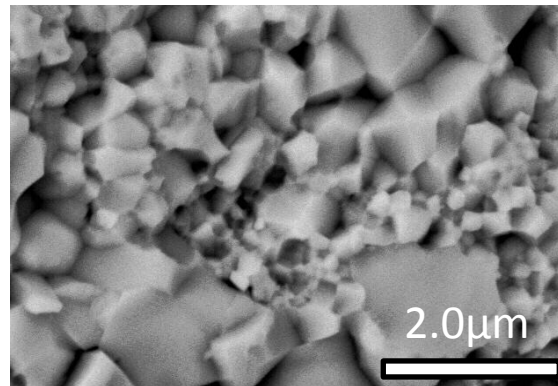
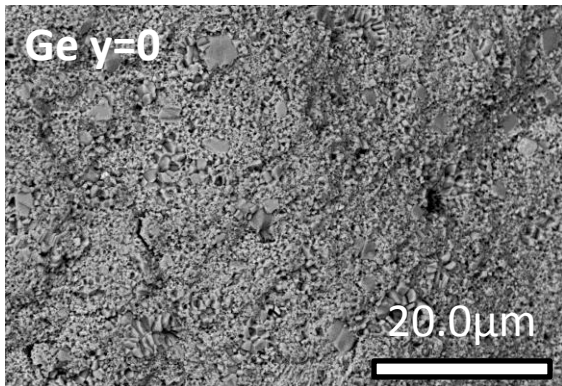
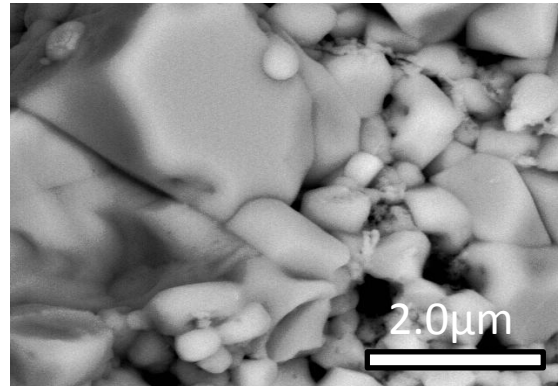
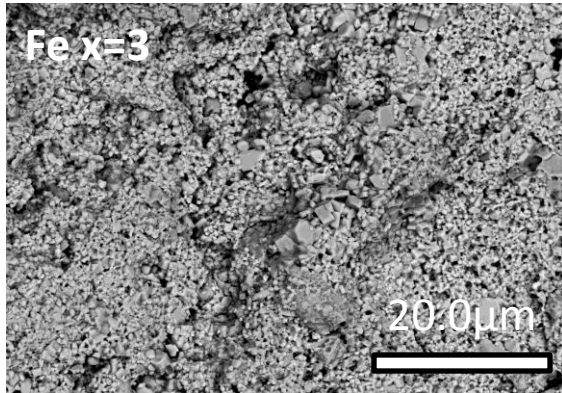


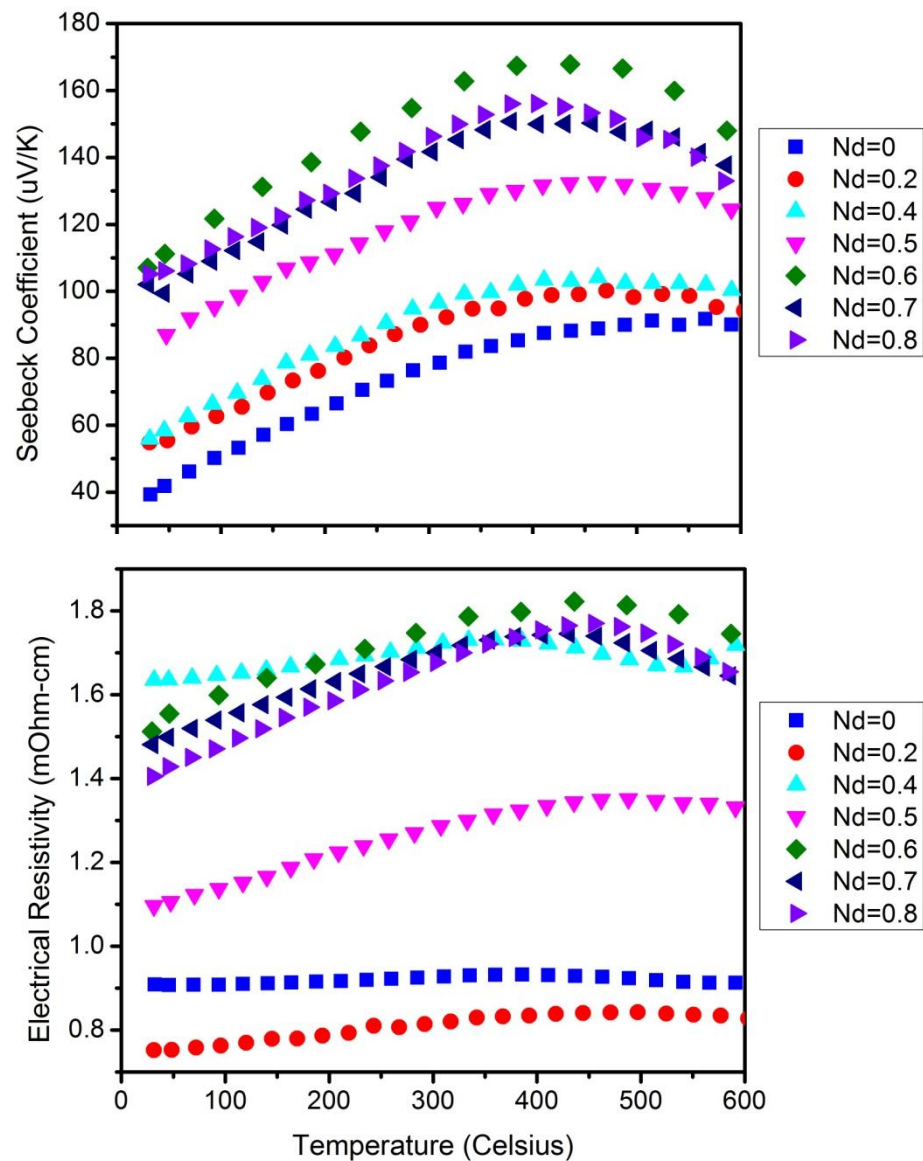
Nominal Composition



Microstructure

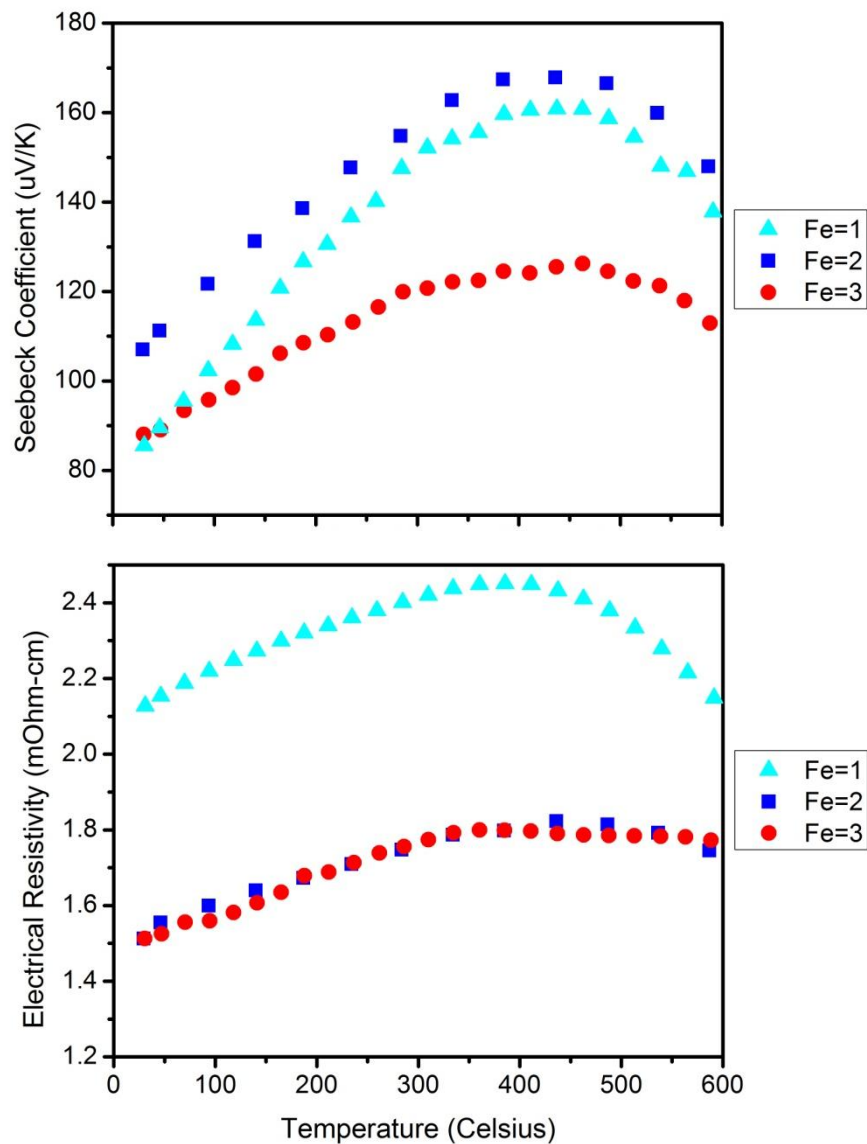
- Similar microstructures for all hot pressed samples, no clear trends for composition.
- Grain size is bimodal with majority of grains 1-2μm, and others as large as 15μm.
- All samples had similar density (>96%) except for the sample with Fe content of 3 (90%).





Seebeck and Resistivity

- Seebeck coefficient trends well with Nd content. Increases with increasing Nd content from 0 to 0.6 then decreases.
- Electrical resistivity does not trend well with Nd content. It trends more with SKD phase purity than Nd content, secondary phases are metallic.
- More phase pure samples ($0.5 < \text{Nd} < 0.8$) had higher electrical resistivity than the less phase pure samples.



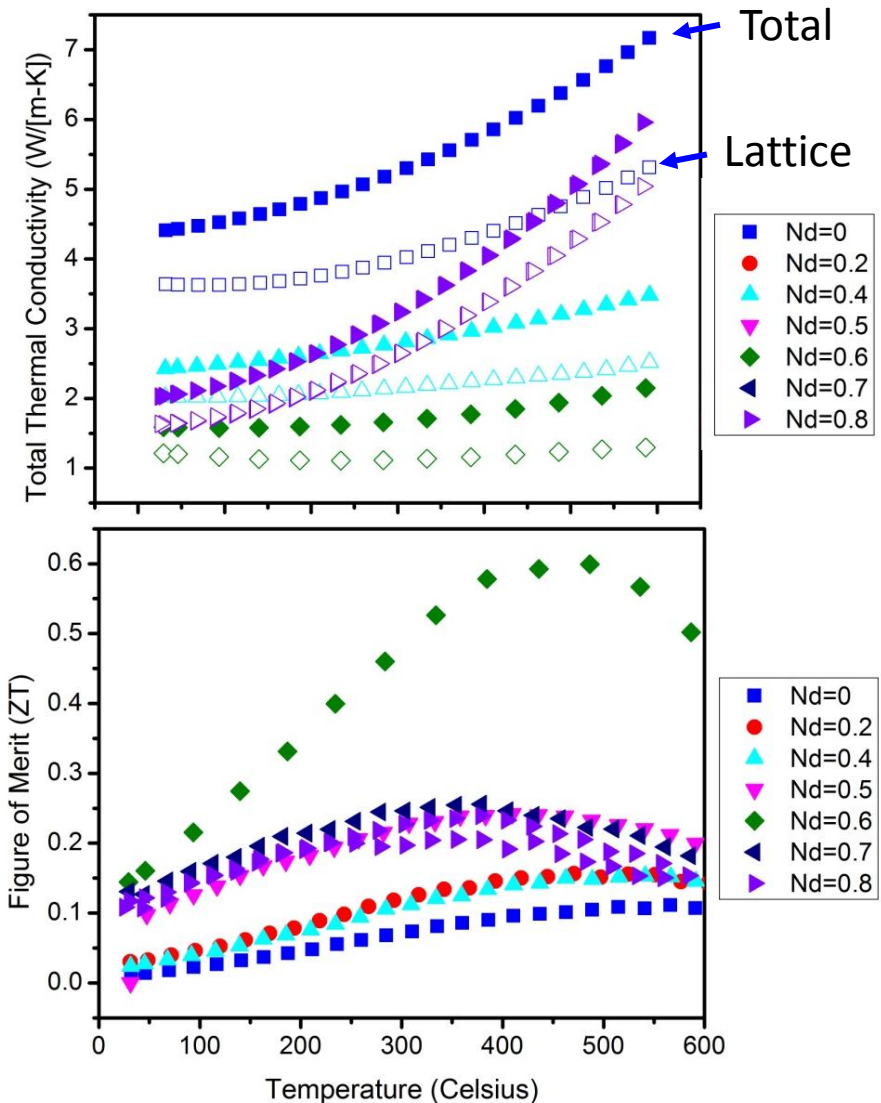
Seebeck and Resistivity

- Seebeck coefficient is maximum for Fe content of 2, slightly lower for 1 and significantly lower for Fe 3.
- Electrical resistivity for Fe 1 is highest, with nearly identical resistivity for both Fe 2 and 3.
- In summary, Power factor is maximum for Fe content of 2 and lower for 1 and 3.



Thermal and Figure of Merit

- Lattice thermal conductivity (open symbols) is calculated using a single parabolic band model.
- Only select samples are shown to avoid crowding the data.
- Lattice conductivity decreases with increasing Nd content up to 0.6.
- Highest ZT is obtained for the Nd 0.6 sample as a result of the low thermal conductivity.
 - The same composition in Zhang's paper reported ZT peak 1.1.

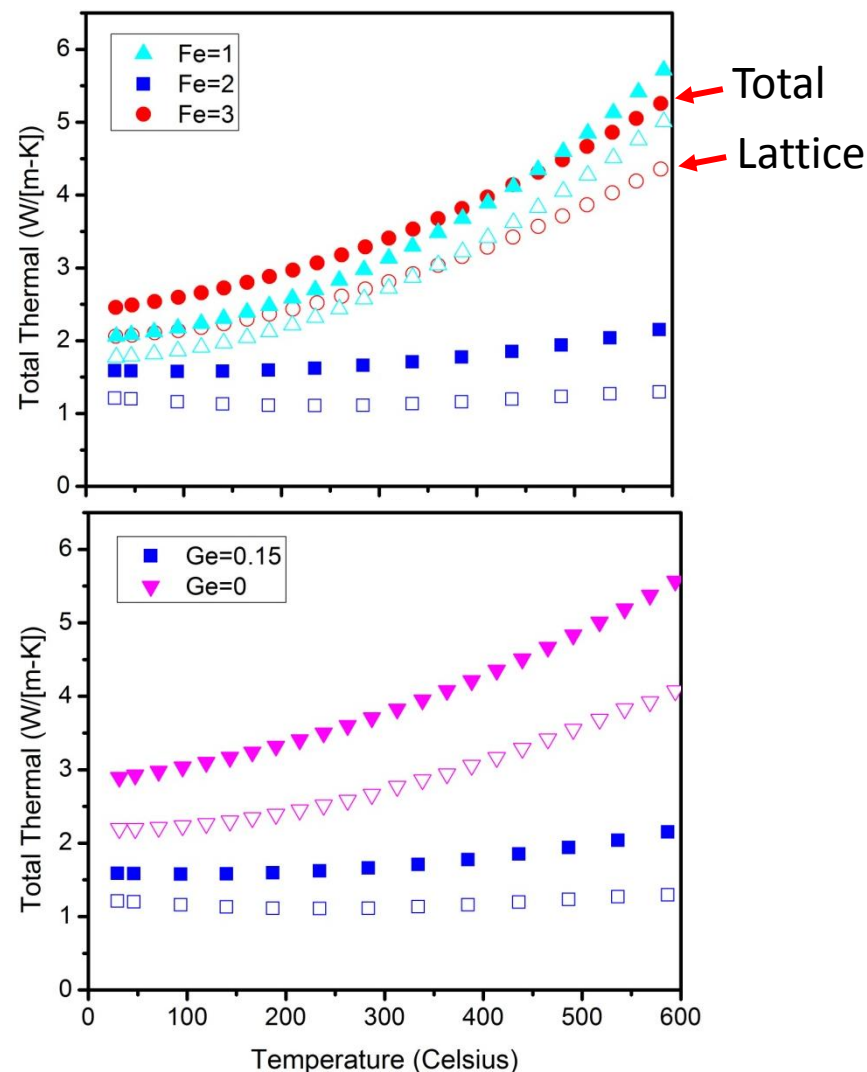


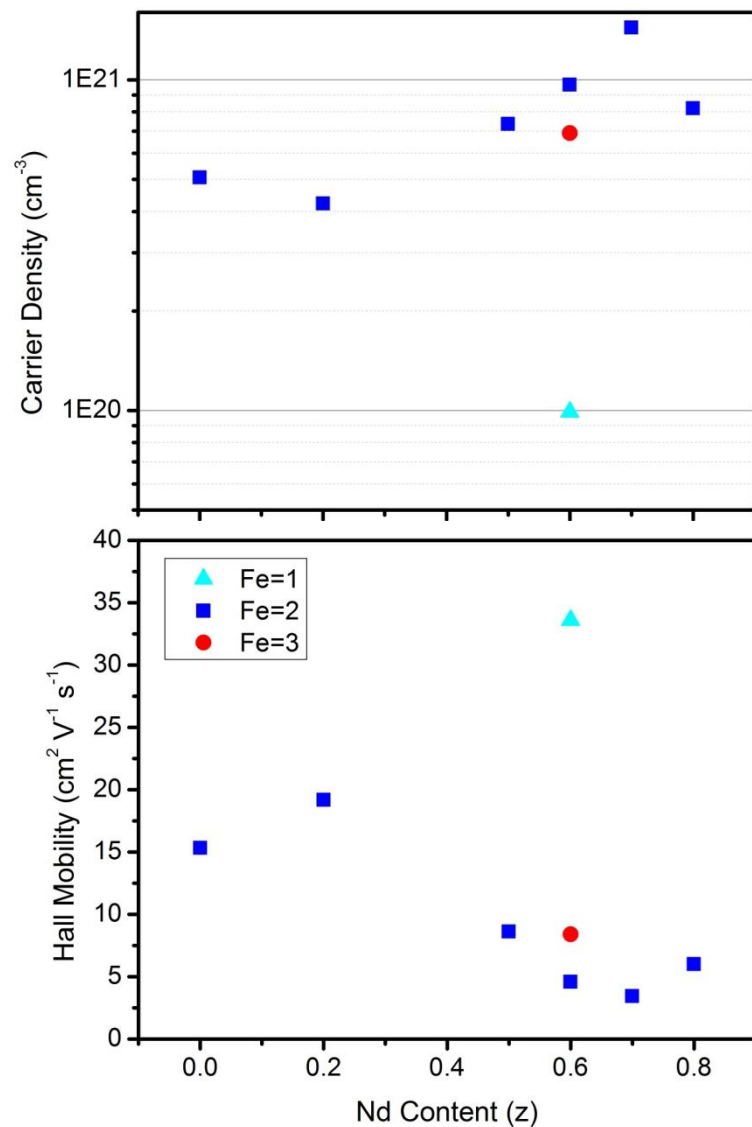


Thermal Conductivity

- Lattice thermal conductivity is minimized for Fe content of 2.
- Fe content of 1 and 3 have similar thermal conductivity.
 - Suggests phonon scattering from Fe-Co bond. Maximized for Fe content of 2.
- Ge reduces lattice component of thermal conductivity.
 - Stronger scattering effect from Ge-Sb bond as Ge content is much lower than Fe content.

Chi *et al.* Phys. Rev. B **86**: 195209 (2012).

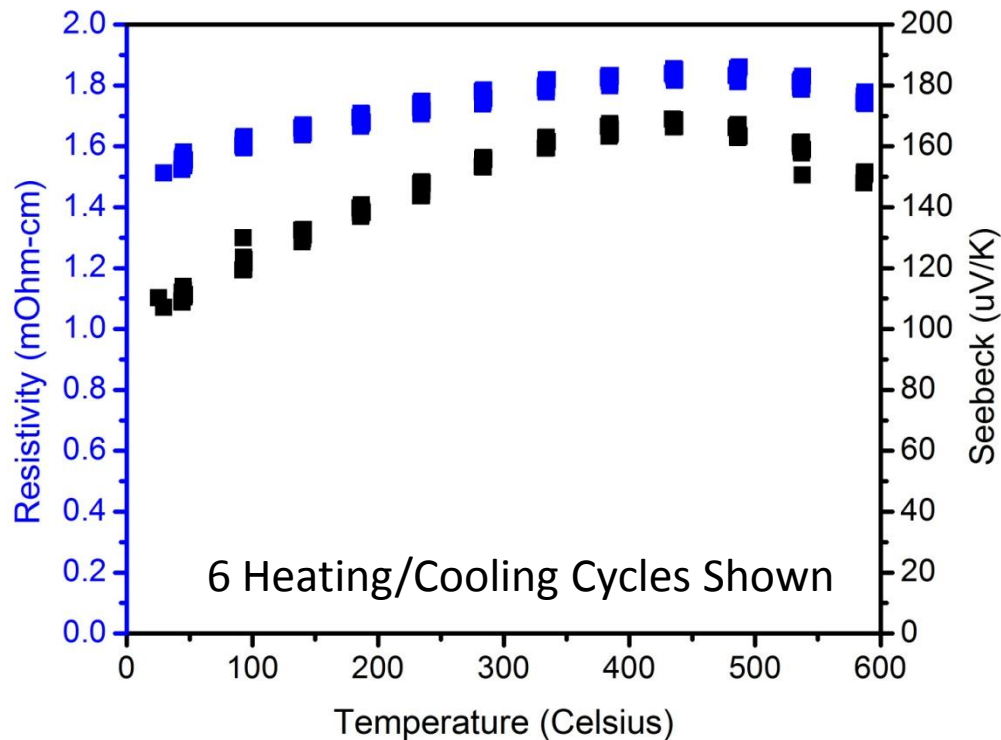




Room Temperature Hall

- Carrier density increases with Nd content up to 0.7, while hall mobility decreases.
- Carrier density and hall mobility show strongest change as a result of Fe content.
 - Hall mobility is minimized and carrier density maximized for Fe content of 2.
 - Fe content of 1 produces the lowest carrier density and highest mobility.
- SPB modeling on the system shows optimal ZT around $2 \times 10^{19} \text{ cm}^{-3}$.

Repeated Electrical Testing



Property Stability

- Electrical properties were tested on slow repeating loops, to investigate phase stability.
- Samples were measured from 25 to 600°C, on 18 hour loops.
- No change observed after 6 cycles.
- XRD of samples annealed at 650°C for 72 hours in N₂ atmosphere showed no change in phase content.

Conclusions

- Fe and Nd content are critical in phase purity of the skutterudite phase, while Ge plays a lesser role.
- Microstructures of hot pressed samples are composed primarily of 1-2 μm grains of SKD with FeSb_2 and Sb phases.
- Electrical and thermal properties are dependant on Nd, Fe, and Ge level.
 - Highest figure of merit was achieved for $\text{Nd}_{0.6}\text{Fe}_2\text{Co}_2\text{Sb}_{11.85}\text{Ge}_{0.15}$ peak ZT 0.6.
 - Published literature reported ZT 1.1 for the same composition.
 - 45% discrepancy may be partially attributed to experimental uncertainty, but not totally.
- Electrical properties and XRD phase are thermally stable.

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